Tracking Drift in WMO Primary CO Standards

Reference to stable CH_4 standard scale

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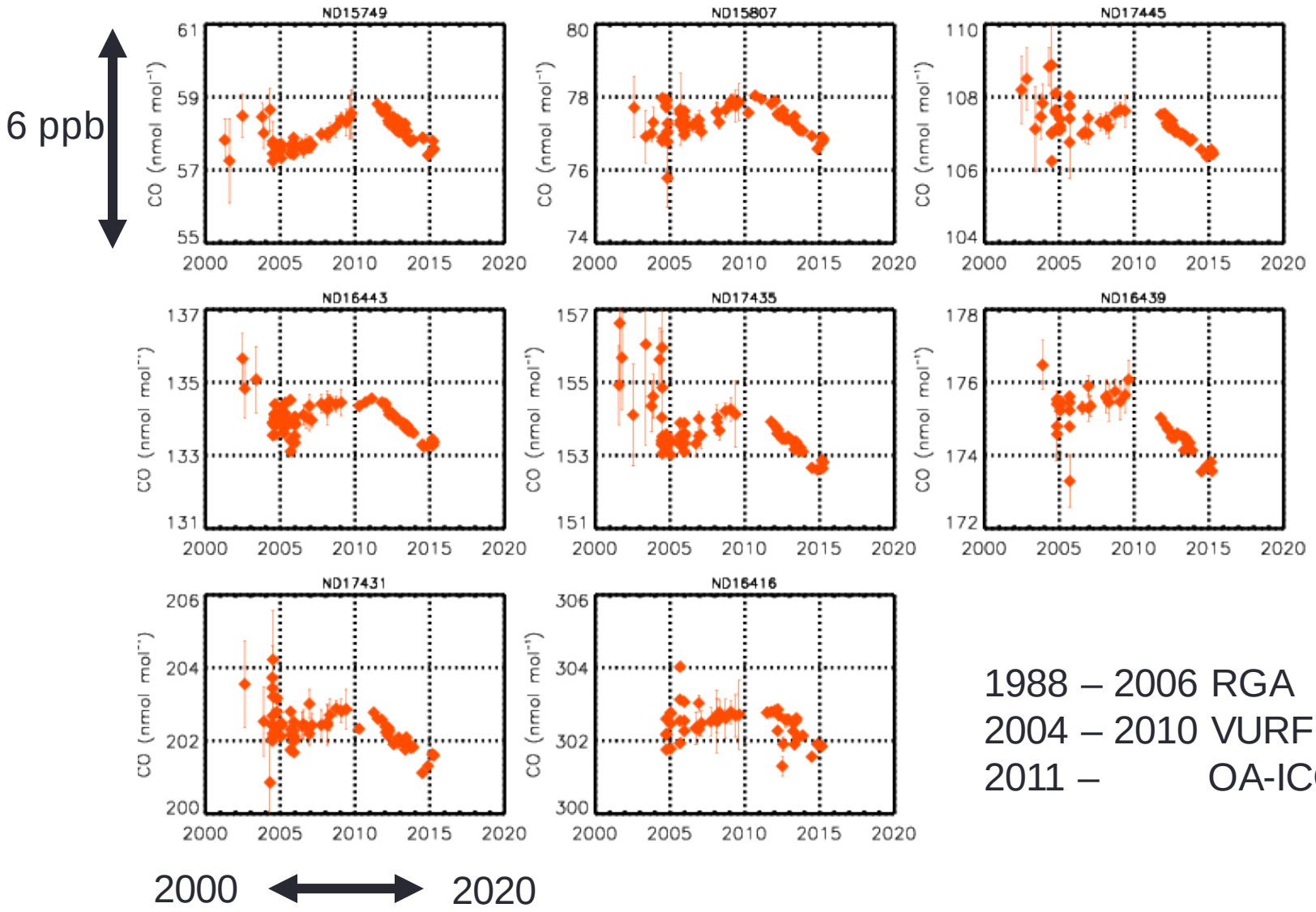
WMO CO Scale

- History:
  - Due to lack of stability in cylinders scale defined by repeated sets of gravimetric standards.
    - 1996/1997, 1999/2000, 2006, and 2011.
  - 2° standards compared to multiple set of gravimetric standards tie the scale together.
- Problems:
  - Gravimetric sets not made frequently enough.
  - 2° standards typically don't last over entire time period.
  - Complex.
- Going Forward (starting in 2012):
  - Simplify definition of the scale:
    - 2011 gravimetric set are the 1° standards.
    - All measurements since 2012 traceable only to the 2011 gravimetric's.
  - Need a method to account for drift in the 1°s

Do we see evidence for drift in the CO scale?



1988 – 2006 RGA
2004 – 2010 VURF
2011 – OA-ICOS

How to track drift in primary standards?

- **Need stable reference point**
  - Percent level gravimetric mixtures of CO, CH_4, and N_2O in air.
    - 0.1 – 0.9% CO
    - 3% CH_4

    CO:CH_4 ratio is known in these parent tanks (± 0.03 – 0.17%).

- **Dilutions of parent mixtures, 3 – 4 times per year**
  - Suite of 12 - 16 dilution standards each
  - Target range: 25 – 1000 ppb CO
  - Uncertainty: 0.2 – 0.6 ppb (1 sigma)

- **Measure CH_4 to determine the CO mole fractions.**
  - Correcting for CH_4 and CO in the diluent gas

- **Determine CO in 1° standards against each suite**
  - Over time, drift should become apparent.
  - 8 episodes since May 2014.
  - Measured on OA-ICOS and VURF instruments.

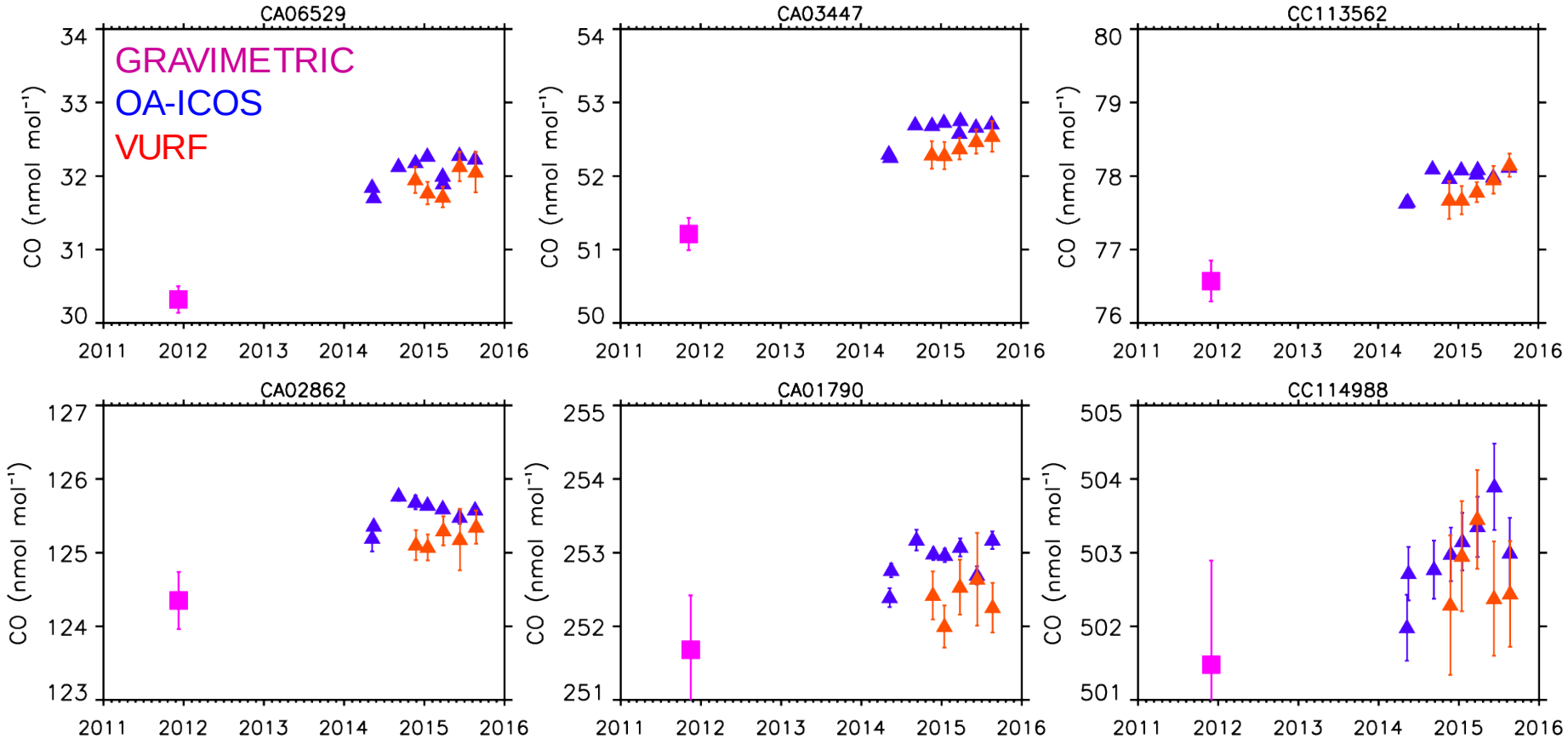
- **Problem:**
  - Started 3 years after the 1° standards were made.
    - Bias not easily distinguished from true drift.
    - Full Suite of gravimetric standards produced in July 2015 to verify method.

CO, CH_4, and N_2O from parents

Parent	CO range (ppb)	CH_4 range (ppb)	N_2O range (ppb)
FB03858	25 - 150	550 – 3515	270 - 830
FB03863	150 - 1100	490 – 3400	250 - 660
FB03885	60 - 190	800 - 1830	325 -415

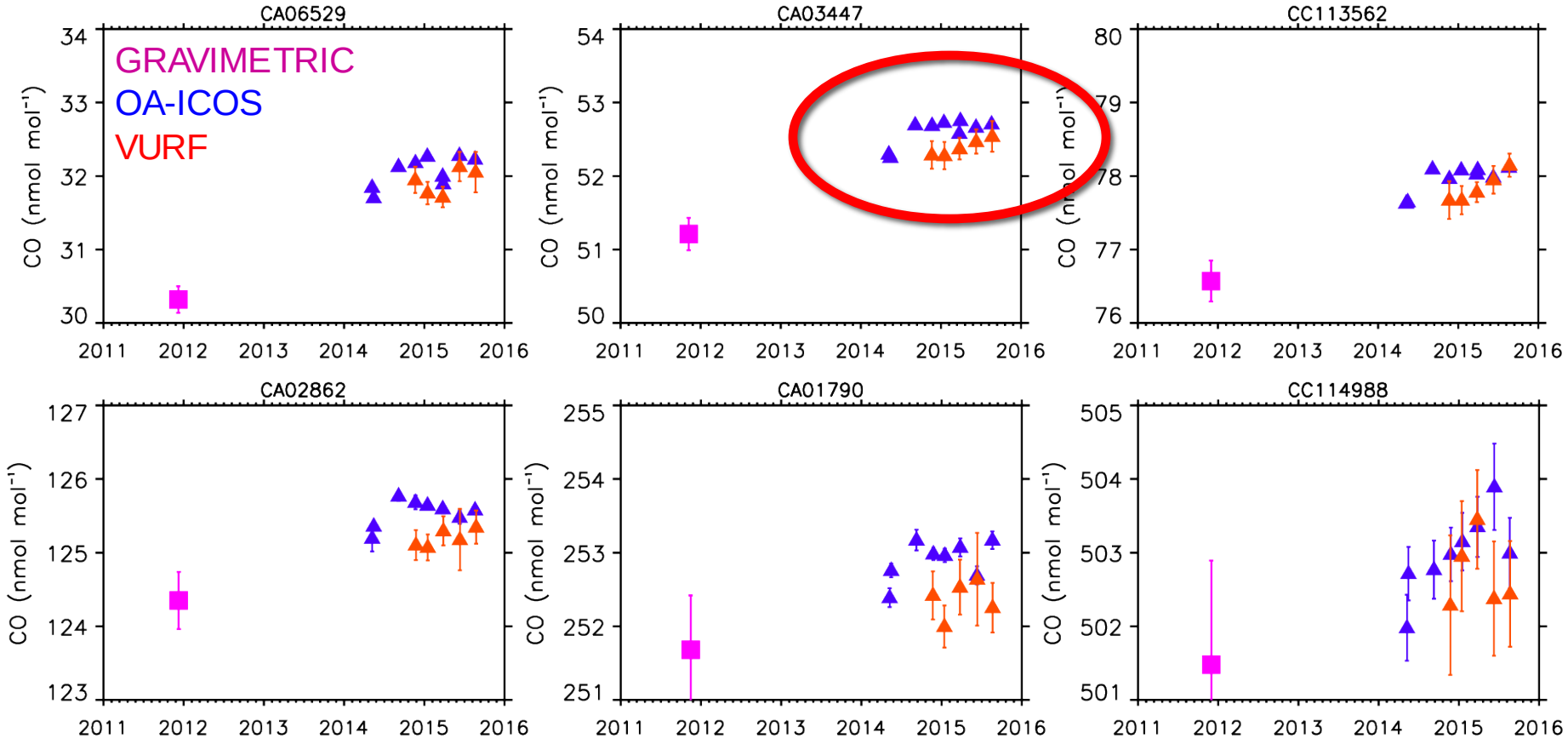
First 5 episodes use parents 1 and 2
Last 3 episodes use parents 1,2, and 3

Results for Primary Standards (6 of 14)



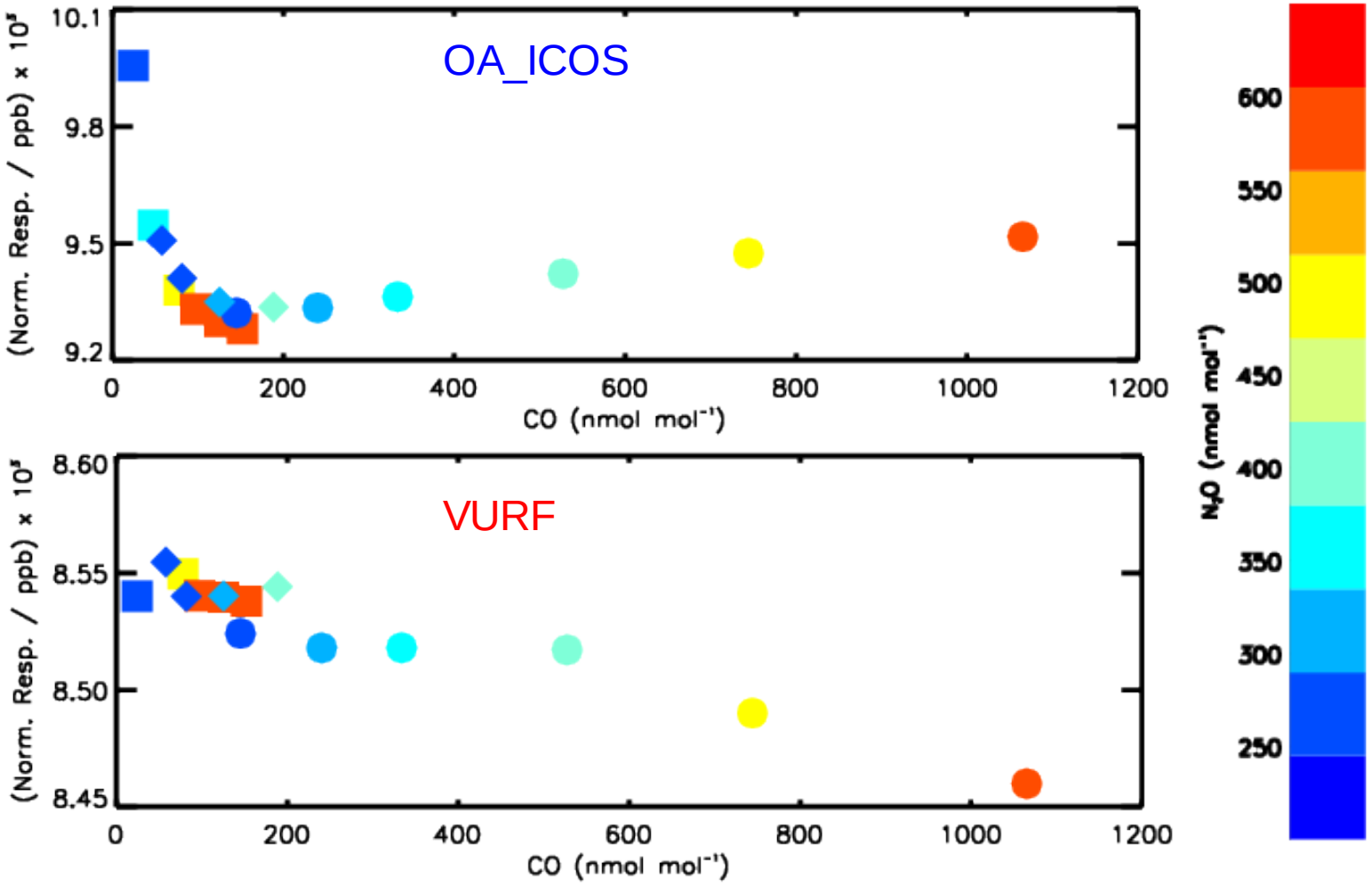
8 calibration episodes since May 2014

Results for Primary Standards (6 of 14)

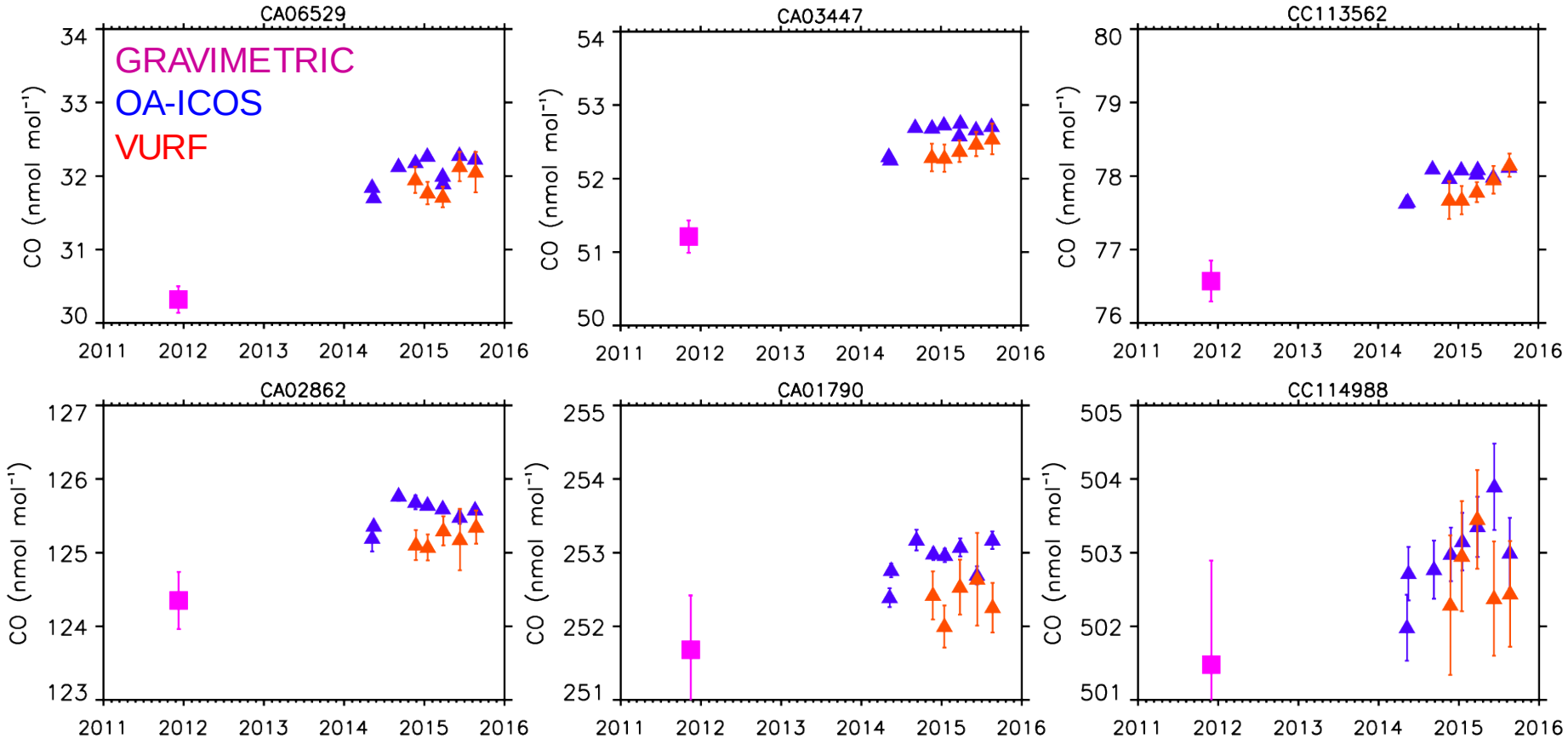


Systematic differences between measurements by OA-ICOS and VURF.

CO offset due to N_2O

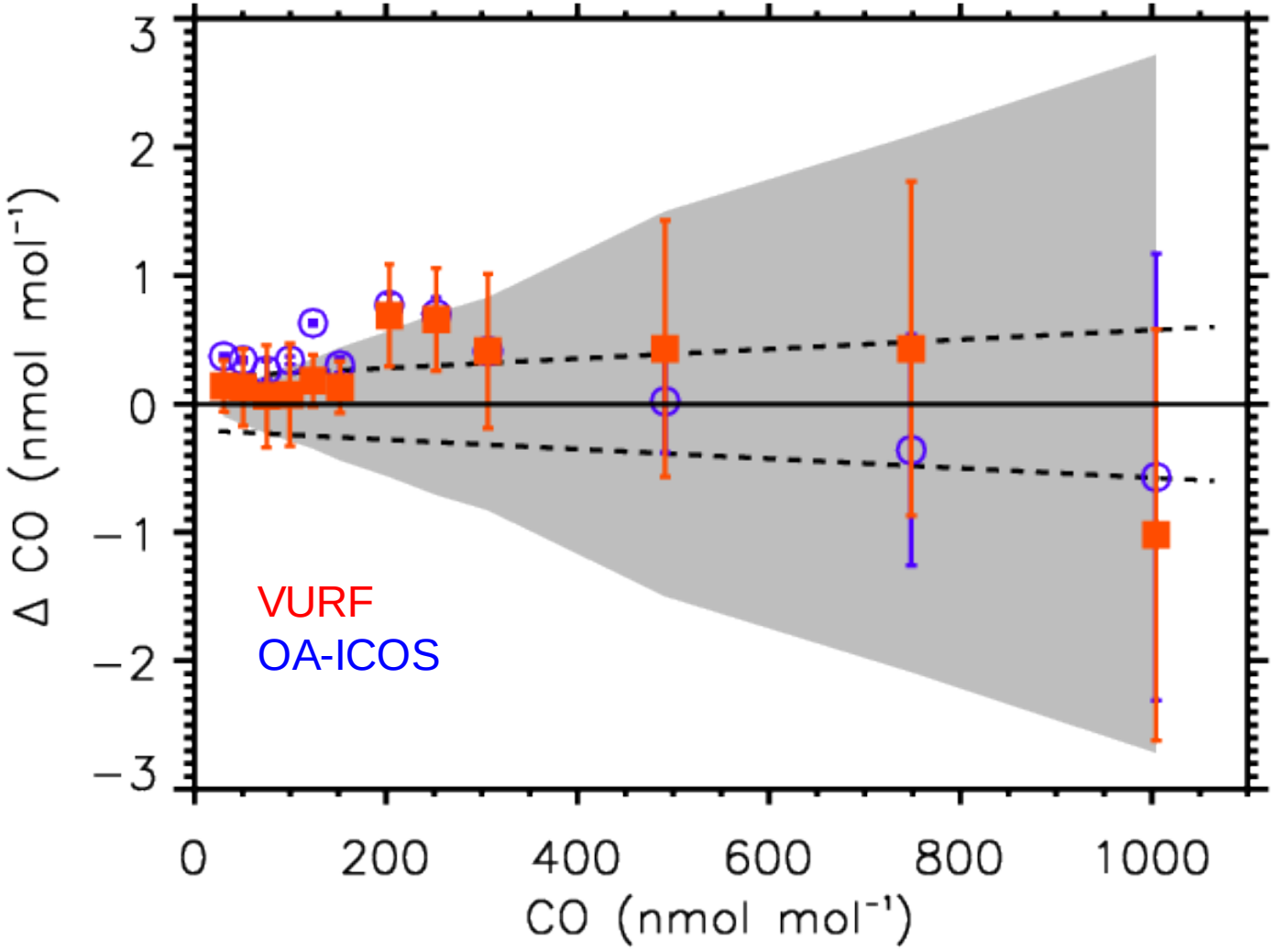


Results for Primary Standards (6 of 14)

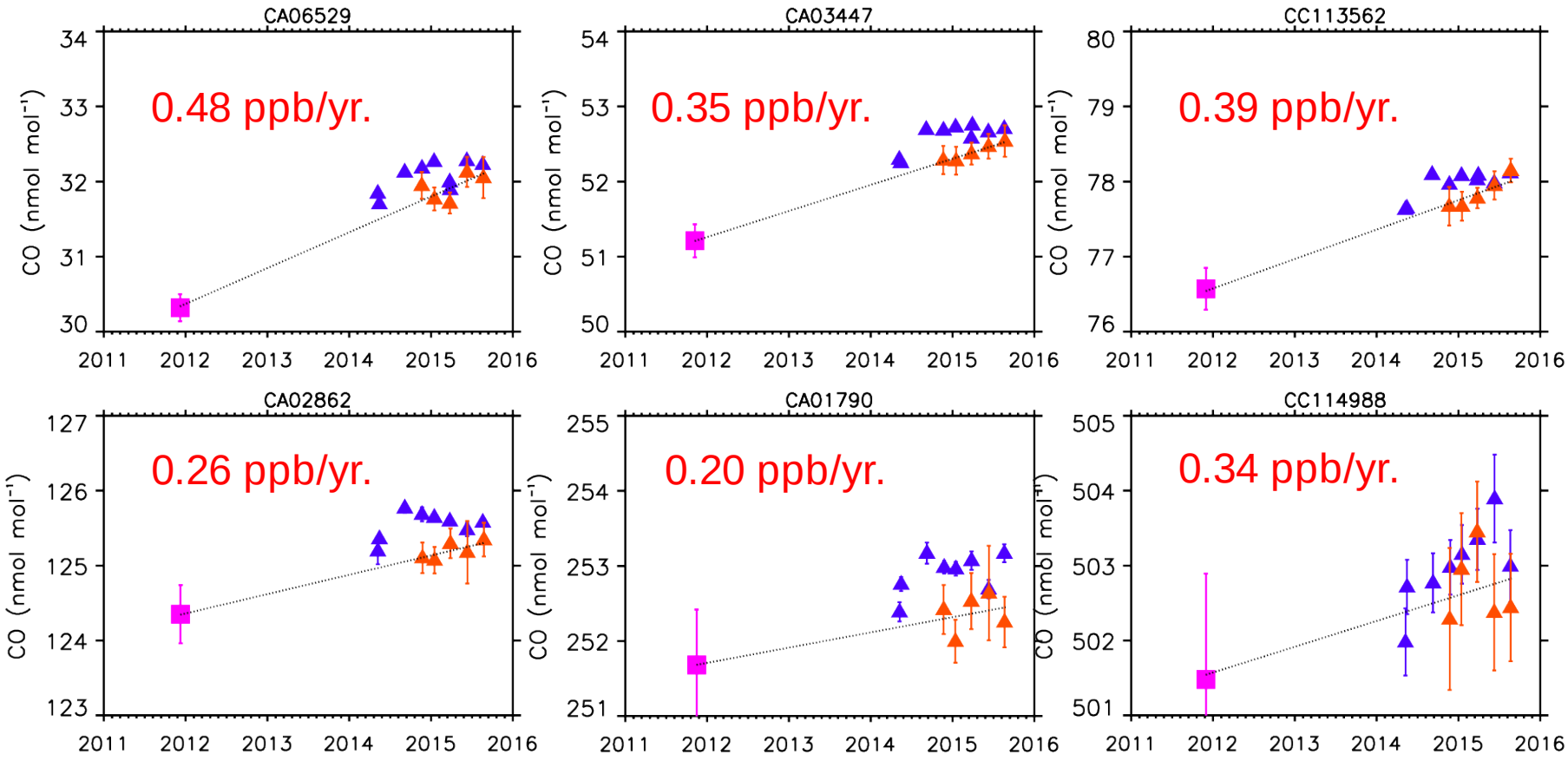


Is there a method bias between the gravimetric standards and dilution standards?

Results for 2015 gravimetric standards



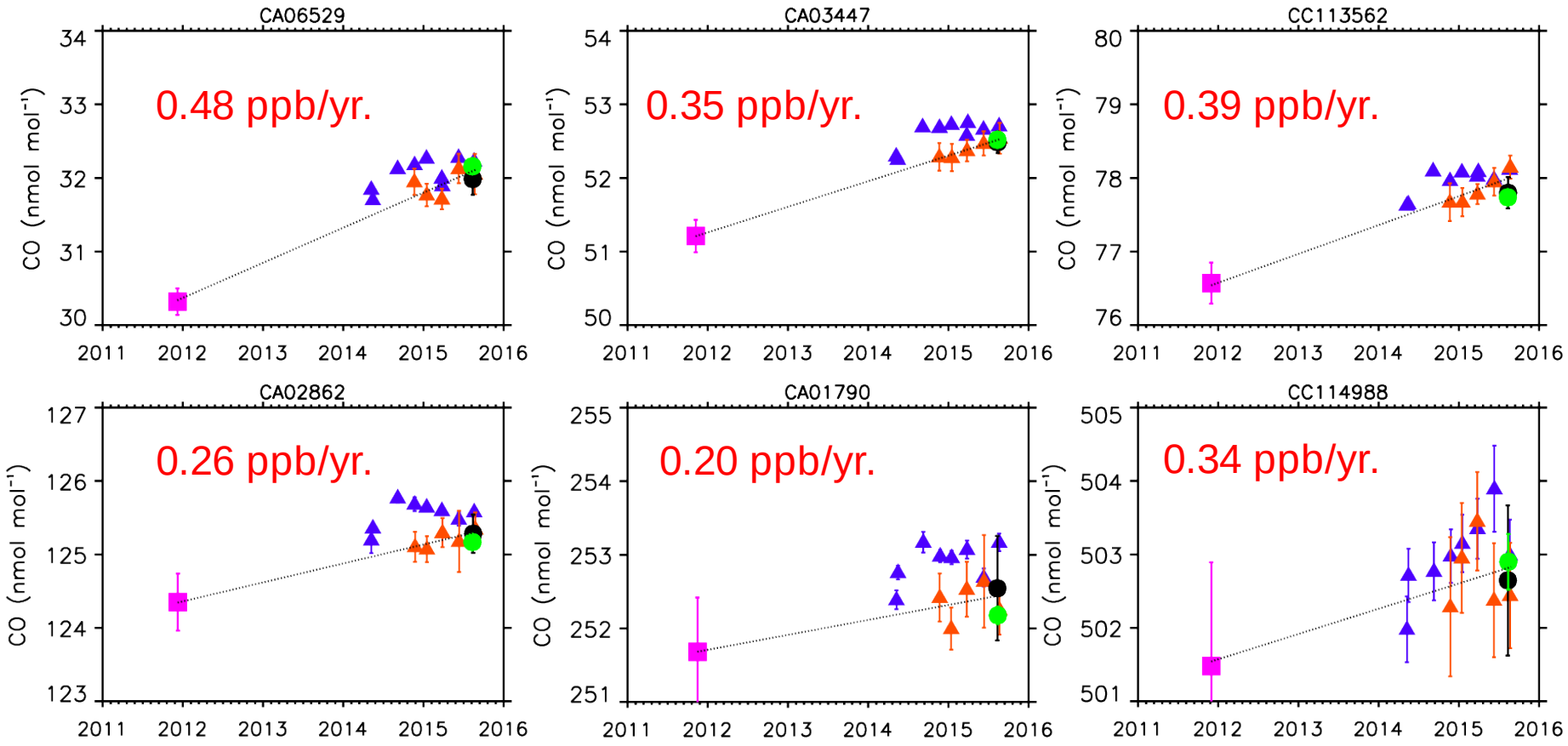
Results for Primary Standards (6 of 14)



GRAVIMETRIC
OA-ICOS vs. Dilution Standards
VURF vs. Dilution Standards

Range of drift rates: 0 – 1.1 ppb/yr.

Results for Primary Standards (6 of 14)



GRAVIMETRIC

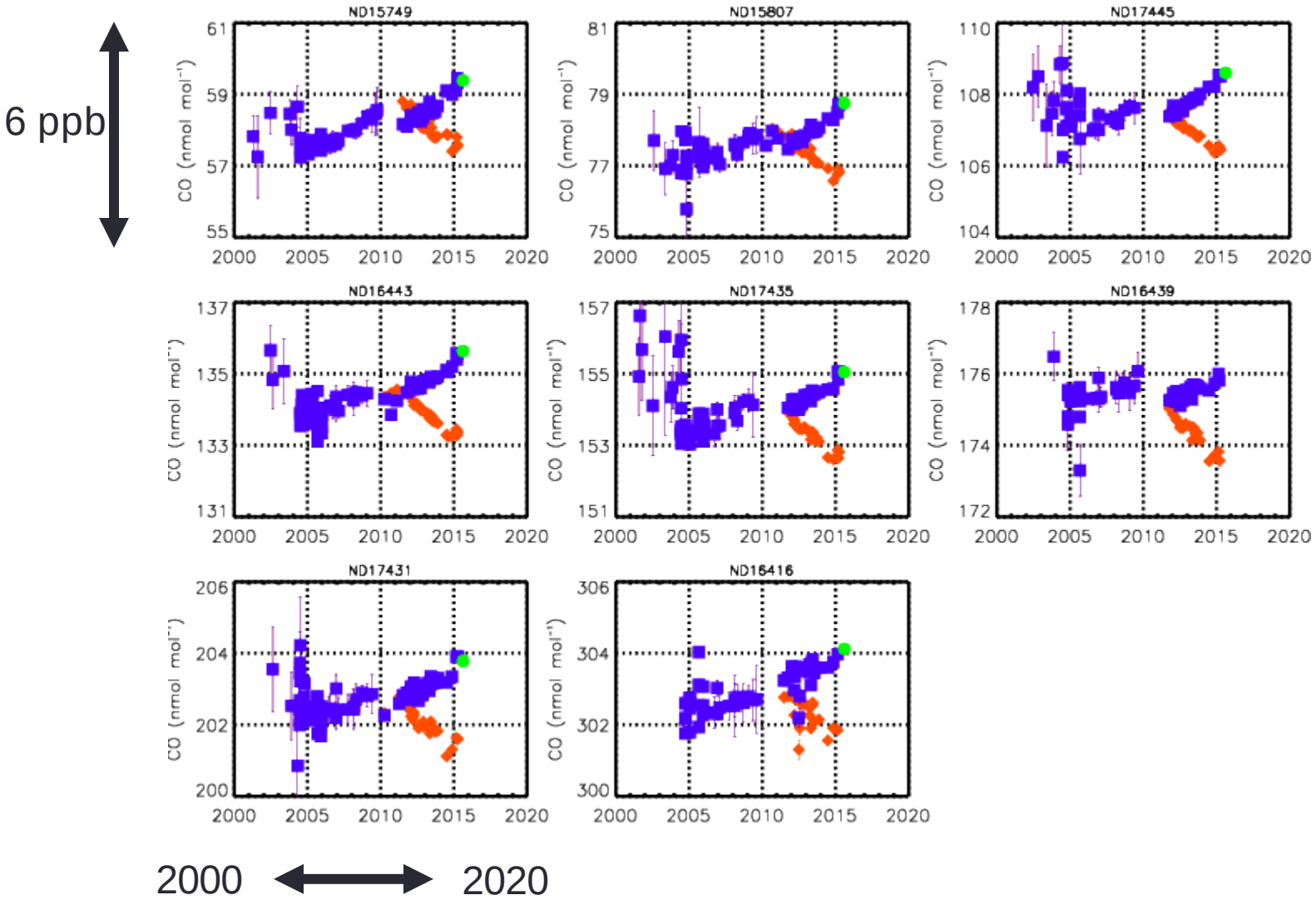
OA-ICOS vs. Dilution Standards

VURF vs. Dilution Standards

OA-ICOS vs. 2015 Gravimetric standards

VURF vs. 2015 Gravimetric standards

Reprocessed Target Tank data



Conclusions / Implementation

- Making progress on a method to track drift in CO 1° standards.
  - A long term solution.
  - Excellent agreement with the 2015 gravimetric standards.

- Implementation:
  - 2011 Gravimetric standards are still the 1°s.
  - Need better uncertainty determinations.
  - CO_X2014A revised scale released in Nov/Dec 2015.
  - Continue monitoring drift with dilution standards.
  - Future revisions when warranted.

Side session to discuss CO on Wed.